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硕 士 学 位 论 文

葡萄糖化学催化法异构为果糖及其分离研究

Study on the Glucose Isomerization and Separation of
Glucose and Fructose

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摘要

随着化石资源的大量消耗,人们普遍意识到需要寻找一种洁净绿色可再生的资源来替代传统资源。其中,生物质被认为是唯一可以替代化石资源获取燃料、化学品和材料的可再生资源。糖类是生物质中最重要的组成部分,使用糖类作为原料可以制得一系列高附加值化学品。近年来,由碳水化合物转化为 5-羟甲基糠醛(HMF)和 2,5-二甲基糠醛(DMF)的研究获得了国内外科学界和工业界的广泛关注,而由碳水化合物中的果糖进行转化相较于以葡萄糖作为原料具有明显优势。相关研究表明,葡萄糖果糖的异构化过程是由葡萄糖脱水形成 HMF 的重要中间步骤,即,果糖是葡萄糖脱水反应的重要中间态,果糖的生成控制了葡萄糖脱水反应生成 HMF 的反应进程。易知,由葡萄糖为原料制备 HMF 的困难程度和复杂程度主要受限于葡萄糖的异构化过程,直接以果糖为原料可以有效降低反应难度。工业上一般使用酶催化法催化葡萄糖果糖的异构化反应,但是生物化学的方法对反应环境的要求较高,不仅要求葡萄糖具有较高的纯度,而且要求反应体系具有适宜且稳定的酸碱条件和反应温度。鉴于生物化学方法的以上缺点,研究者们将目光投向了对反应条件要求较为宽泛的化学催化法,以期在容易控制的实验条件下得到高的葡萄糖转化率和果糖得率。本论文以绿色化学理念为宗旨,以碳水化合物为原料,针对目前葡萄糖果糖异构化过程中存在的问题开展了一系列研究,包括绿色、高效、价格低廉和制备方法简单的催化剂的开发以及葡萄糖果糖的有效分离纯化,并取得了一定的研究成果。

首先,在本实验中以实验室常见的金属盐类作为考察对象,其对葡萄糖果糖的异构化反应均具有良好的催化效果,但是均相催化剂的回收复用步骤比较繁琐。同时,在本实验中采用了单因素变量法研究反应温度、反应时间、催化剂的量对异构化反应的影响并以此来优化化学均相催化剂制备果糖的反应条件。通过单因素实验变量,最终确定了 NaAlO_2 催化葡萄糖异构化反应的最佳工艺条件:反应温度为 55°C , 反应时间为 3 h, 催化剂用量 1.0 g (Cata./Glu.=1: 5), 最终得到反应得率为 44.57%。

其次, 在本实验中研究了一系列的非均相催化剂, 诸如三元金属类水滑石以及由各类分子筛负载偏铝酸钠的非均相催化剂等。在由各类分子筛负载偏铝酸钠的非均相催化剂中, HY 分子筛负载后的催化效果优于其他分子筛复合催化剂。负载后的 HY 催化剂能够重复利用至少五次并仍具有催化效果。

同时, 三元金属类水滑石催化剂 Mg-Al-Sn, Mg-Al-Zn, 和 Mg-Al-Cu 也作为非均相催化剂应用到葡萄糖果糖的异构化反应中。其中, Mg-Al-Zn 催化剂在反应温度为 90 °C, 反应时间为 3 h 条件下得到 61.07% 的葡萄糖转化率以及 27.30% 的果糖得率。不过, 三元金属类水滑石催化剂的回收复用步骤较为繁琐, 实用价值低于偏铝酸钠负载型分子筛催化剂。

接着, 上文所述的非均相催化剂使用扫描电镜 (SEM)、X-射线衍射 (XRD)、傅里叶变换红外光谱 (FT-IR)、X 射线光电子能谱 (XPS)、比表面积 (BET) 以及程序升温脱附 (TPD) 等手段对其进行了详细表征。与传统的非均相催化剂相比, 负载后的分子筛催化剂具有更高的催化活性。

在上述研究的基础上, 在反应投料为 1.0 g 葡萄糖, 1.0 g AlO_2^-/HY 催化剂以及 15.0 g 去离子水, 反应温度为 55 °C, 反应时间为 3h 的条件下得到了 60.21% 的葡萄糖转化率以及 43.43% 的果糖选择性。重复使用五次之后, 葡萄糖选择性以及果糖得率均未见明显降低。

最后, 根据离子交换树脂对于葡萄糖和果糖吸附能力的不同, 葡萄糖果糖混合液可通过离子交换树脂进行分离。利用高效液相色谱 (HPLC) 对分离纯化得到的果糖进行了确认, 并证实了它的物理性质如折光性, 水溶性和外观等与纯品基本一致。

关键词: 果糖; 葡萄糖异构化; 非均相催化剂; 分离

Abstract

In recent years, biomass is considered to be the only renewable resources in nature to replace the fossil resources for the production of fuels, chemicals and materials. The conversion of carbohydrates that are the most abundant components of biomass into 5-hydroxymethylfurfural (HMF) and 2, 5-dimethylfuran (DMF) is one of the most important pathways for the utilization of biomass, which has attracted much attention in the domestic and international scientific and industrial communities. Industrially, enzymes are usually used in the isomerization of glucose into fructose, but biological catalyst also suffers from many drawbacks for it requires high glucose purity and a narrow limited operating pH and reaction temperature. In view of the above mentioned drawbacks of the biological catalysts, researchers have put a lot of efforts to develop chemical routes to catalyze glucose isomerization which possess the advantages of easily-operating conditions and high conversion of glucose. According to the current research situation and existing problems for the isomerization of glucose into fructose, a series of studies persisted in the concept of green chemistry were carried out in this dissertation, for example, the development of green, efficient, low-cost and easily prepared catalysts, the establishment of heterogeneous reaction systems and the separation and purification of fructose syrup.

Firstly, NaAlO_2 and lots of homogeneous catalysts was found efficient to catalyze glucose isomerization, but it can't be used repeatedly. Furthermore, the effects of reaction temperature, reaction time, catalyst loading on the isomerization and the optimal reaction conditions were investigated by single factor method. Excellent yield of fructose were achieved under the following reaction condition: 5 g glucose, 1g catalyst, 90°C , 3 h.

Secondly, zeolites modified by NaAlO_2 were found efficient to catalyze glucose isomerization. Series of modified zeolite catalysts were examined as catalysts in the isomerization of glucose into fructose. Among these catalysts, the one based on HY zeolite and sodium aluminate was more preferable than others. A glucose conversion

of 60.21% and a fructose selectivity of 43.43% were obtained when the temperature was 55°C with a reaction time of 3h. The modified HY catalyst could be reused at least five times while no significant loss of catalytic activity was observed. Excellent yields of fructose were achieved under the following reaction conditions: 1g glucose, 1g catalyst and 15g deionized water, 90°C, 3 h. After five successive runs, zeolites modified by NaAlO₂ still remained excellent catalytic activity. Mg-Al-Sn, Mg-Al-Zn, and Mg-Al-Cu were also found to be effective catalyzing glucose isomerization, while these hydrotalcite-like compounds can't be used repeatedly.

Subsequently, Mg-Al-Sn, Mg-Al-Zn, and Mg-Al-Cu and zeolites modified by NaAlO₂ were well characterized by Scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Branauer-Emmett-Teller surface area (BET) and Adsorption Temperature Programmed. Compared with conventional catalysts, such as ion-exchange resin, Mg-Al hydrotalcite, metal oxides and zeolite catalysts, the modified catalysts were more effective for the isomerization of glucose into fructose.

On the basis of the above-mentioned studies, the mild reaction system for the isomerization of glucose into fructose was developed 60.21% glucose conversion and 43.43% fructose selectivity could be obtained under the following reaction conditions: 1g glucose, 1g catalyst (HY zeolite modified by NaAlO₂) and 15g deionized water, 90 °C, 3 h. After five successive runs, the loss of NaAlO₂ had little effect on glucose conversion, resulted in a slight decrease in the yield of fructose.

Finally, according to the different absorption ability of the glucose and fructose of ion exchange resin, fructose was separated and purified from glucose by ion exchange resin. The chemical structure of purified fructose was confirmed by High performance liquid chromatography (HPLC) and Nuclear magnetic resonance spectroscopy (NMR), and its physical properties such as refractive index, water solubility and appearance of purified fructose was verified to be consistent with pure fructose.

Keywords:: Fructose; Glucose isomerization; Heterogeneous catalyst; Separation

目 录

摘要.....	I
Abstract.....	III
第一章绪论	1
1.1 引言	1
1.2 生物质	1
1.3 果糖及其应用	2
1.3.1 果葡糖浆及果糖.....	2
1.3.2 果糖的应用.....	3
1.4 果糖的制备	6
1.4.1 均相催化体系.....	7
1.4.2 非均相催化体系.....	8
1.4.3 果糖的生产方法.....	10
1.4.4 果糖与葡萄糖的分离.....	11
1.5 果糖生产中存在的问题	13
1.5.1 葡萄糖的异构化.....	13
1.5.2 果糖和葡萄糖的分离.....	13
1.6 本论文的选题意义及研究内容	14
1.6.1 本论文的选题意义.....	14
1.6.2 本论文的研究内容.....	15
第二章均相催化剂偏铝酸钠催化葡萄糖异构化为果糖的研究.....	16
2.1 引言	16
2.2 材料与方法	17
2.2.1 实验材料.....	17
2.2.2 实验仪器与设备.....	17
2.2.3 葡萄糖果糖的异构化反应.....	17
2.2.4 产物分析.....	18

2.3 结果与讨论	20
2.3.1 不同催化剂催化活性的比较	20
2.3.2 单因素变量	22
2.4 本章小结	26
第三章非均相体系中化学法催化葡萄糖异构化为果糖的研究	28
3.1 引言	28
3.2 材料与方法	28
3.2.1 实验材料	28
3.2.2 实验仪器与设备	29
3.2.3 催化剂的制备	29
3.2.4 实验步骤	29
3.2.5 产物分析	30
3.2.6 催化剂的表征	32
3.3 结果与讨论	33
3.3.1 不同非均相催化剂催化活性的比较	33
3.3.2 AlO_2/HY 负载型催化剂的催化效果	35
3.3.3 催化剂表征	37
3.4 本章小结	45
第四章离子交换树脂分离葡萄糖和果糖的研究	46
4.1 引言	46
4.2 材料与方法	46
4.2.1 实验材料	46
4.2.2 实验仪器与设备	46
4.2.3 实验方法	47
4.2.4 产物分析	48
4.3 结果与讨论	50
4.3.1 温度的影响	50
4.3.2 上样量的影响	51
4.3.3 洗脱速度的影响	53
4.3.4 上样浓度的影响	54

4.3.5 回收树脂的吸附性能.....	55
4.4 本章小结	56
结论与展望	57
附录.....	59
攻读硕士学位期间取得的研究成果	61
致谢.....	73
参考文献	62

厦门大学博士论文摘要库

Table of Contents

Chinese abstract.....	I
English abstract.....	III
Chapter 1 General introduction	1
1.1 Introduction.....	1
1.2 Biomass.....	1
1.3 Fructose and fructose application	2
1.3.1 Fructose.....	2
1.3.2 The application of fructose	3
1.4 Preparation of fructose.....	6
1.4.1 Homogeneous reaction system	8
1.4.2 Heterogeneous reaction system.....	10
1.4.3 The preparation of fructose	11
1.4.4 The separation of glucose and fructose.....	13
1.5 Problems about fructose preparation	13
1.5.1 The isomerization of glucose	13
1.5.2 The separation of glucose and fructose.....	14
1.6 Research significance and main contents	14
1.6.1 Research significance.....	15
1.6.2 Main contents.....	16
Chapter 2 Chemical catalysis of glucose isomerization under homogeneous reaction system.....	17
2.1 Introduction.....	17
2.2 Materials and methods	17
2.2.1 Experiment reagents.....	17
2.2.2 Experiment apparatus.....	18

2.2.3 Glucose isomerization.....	20
2.2.4 Products analysis.....	20
2.3 Results and discussion	22
2.3.1 Comparison of different catalysts	28
2.3.2 Single factor reaction	28
2.4 Conclusions.....	28
Chapter 3 Chemical catalysis of glucose isomerization under heterogeneous system.....	28
3.1 Introduction.....	28
3.2 Materials and methods	28
3.2.1 Experiment reagents.....	28
3.2.2 Experiment apparatus.....	28
3.2.3 The preparation of catalyst.....	28
3.2.4 Reaction procedures.....	30
3.2.5 Characterization of heterogeneous catalyst	32
3.3 Results and discussion	33
3.3.1 Results analysis.....	33
3.3.2 Catalyst characterization	35
3.3.3 Investigation of reaction parameter	37
3.4 Conclusions.....	45
Chapter 4 Separation of glucose and fructose	46
4.1 Introduction.....	46
4.2 Materials and methods	46
4.2.1 Experiment reagents.....	46
4.2.2 Experiment apparatus.....	47
4.2.3 Reaction procedure	48
4.2.4 Product analysis	50
4.3 Results and discussion	50
4.3.1 Effect of reaction temperature.....	51
4.3.2 Effect of syrup quantity	53

4.3.3 Effect of flow velocity	54
4.3.4 Effect of syrup concentration	55
4.3.5 Adsorption capacity of recycled resin	56
4.4 Conclusions	57
Conclusions and prospects	59
Appendix	60
Author`s publications	61
Acknowledgement	62
References	63

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